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Environmental Leverage Inc.
Turning Liabilities into Leverage

Biological Nutrient Removal vs. Chemical Nutrient Removal

Many municipalities are being forced to remove nutrients, specifically nitrogen as well as phosphorus.
Phosphorus regulations currently are tighter in most places than nitrogen. Some places are forced to nitrify, or remove ammonia and convert it to nitrates. Some places actually have total N as a final effluent permit.

There are numerous ways to achieve nutrient removal. Biological is the most common way. Chemical removal of phosphorus is slowly being added to most municipal treatment plants in their plant upgrade planning stages. BNR or luxury biological nutrient removal is a harder, more complicated process and requires more than one stage to achieve nutrient removal with various species of bacteria.

Let's go over the options:
Normal Wastewater treatment
Nitrification / Denitrification
Biological Nutrient removal
Alum/Ferric precipitation

Normal wastewater treatment will remove quite a bit of nutrients. **100-5-1** for every 100 parts of carbon in the influent 5 parts of ammonia and one part of phosphorus should be used by normal floc forming bacteria, so you can almost do a math balance on how many nutrients will be taken up the easy way. Keep in mind we said normal floc formers. Zoogleal bacteria do not take up many nutrients; they actually thrive in nutrient deficient conditions. Some Filamentous bacteria thrive in nutrient deficient conditions, so make sure you select for the bacteria in your plant that will achieve the most and help with your plants requirements.

How to do the Total Math for N in a biological system

Influent---- Aeration Basin------Effluent

TKN (Amines and NH3)
Nitrates
Nitrites

BOD removal will remove 5 ppm NH3 per each 100 ppm- remainder has to be consumed by nitrification

TKN, NH3 plus Nitrates and Nitrates should equal total influent number minus BOD correlation

Influent Example
BOD- 300
TKN-75
NH3-35
Nitrates-0
Nitrites-0

Since the BOD degraders consume
15 ppm N as a nutrient source-
   300 ppm BOD/100 *5=15
60 ppm would be left for nitrification

Final Effluent Example
BOD- 3
TKN-0
NH3-.005
Nitrates-56
Nitrites-4

**Therefore, that means there are 35 parts in the TKN as NH3 and the rest are amines- 40 PPM

** Always make sure you measure Solids dewatering supernatant as well as digestor supernatant.
They are often overlooked in the total math analyses.

Nitrification:
If you have additional ammonia in the influent, you can use nitrification to convert ammonia to nitrates.
Most permits have an ammonia level, due to the fact that ammonia in high levels is toxic to fish.
We have numerous newsletters just on nitrification, so if you have problems with nitrification, amines in the influent, TKN, etc. please let us know, and we can email those specific newsletters to you.
Many people do not understand that it is a completely different

process and completely different species that perform nitrification. Carbonaceous bacteria use the carbon as a food source. Nitrosomonas and Nitrobacter use carbonate as their food source and the ammonia is just their energy transfer source. They do not "eat" the ammonia. Most of the NH3-N is used as an energy source. It is used in a non-assimilative way so only a small amount of biomass (sludge) is produced. Carbon dioxide (CO2) or carbonate is used as the carbon source in nitrification. That is why alkalinity is extremely critical in nitrification. 7.14 parts of alkalinity are required for each part of ammonia to be removed.

The Nitrification Process
First Conversion (Ammonium to Nitrite)
Nitrosomonas bacteria oxidize ammonium to nitrite via hydroxylamine.

$$2NH_4^+ + O_2 \longrightarrow 2NH_2OH + 2H^+$$
$$NH_4^+ + 1.5\ O_2 \longrightarrow NO_2^- + 2H^+ + H_2O$$
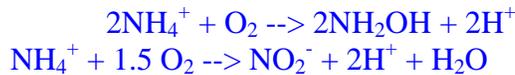
Second Conversion (Nitrite to Nitrate)
Nitrobacter bacteria convert nitrite to nitrate.

$$NO2- + 0.5\ O2 \longrightarrow NO3-$$

Nitrification also occurs 3-4 times slower than carbonaceous oxidation. Upsets to a plant can take nitrifiers weeks to recover for nitrification as opposed to days or hours for carbon bacteria. For each 1-gram of NH3-N oxidized to NO3, 0.15 grams of new bacteria cells are formed. Sludge generation from nitrifiers is minimal.

Oxygen levels are also critical for nitrification. Higher levels of oxygen are required for nitrification than for carbon removal. As ammonia is removed it is transformed. 4.5 parts of O2 are needed for every part of NH3 to be degraded.

Controlling Factors for Nitrification:
Dissolved Oxygen
Alkalinity (pH)
Wastewater Temperature
Nitrogenous Food
Detention Time
MCRT, F/M, or Sludge Age
Toxic Materials

Permissible pH range (95%)	**7.2 - 9.5**
Permissible Temp (95%)	**60 - 95 degrees F**
Optimum Temp	**85 degrees F**
DO level at peak flow	**>1.0 mg/L**
Heavy Metals	**<5 mg/L**
Toxic Organics	
Halogenated Solvents	**0 mg/L**
Phenol and Cresol	**<20 mg/L**
Cyanides	**<20 mg/L**
Oxygen Requirements	**4.5 lb O2/lb NH3-N**

Dissolved Oxygen requirements for Nitrification-
Nitrification has a substantial oxygen requirement. 4.5 lb O2 is required per lb NH4+-N to be converted. Aeration Tank D.O. usually maintained 1.0 to 4.0 mg/L.

pH, Alkalinity requirements for Nitrification
Nitrification rates are rapidly depressed as the pH is reduced below 7.0. pH levels of 7.5 to 8.5 are considered optimal. Typical refineries run at a pH of 8-9 with no problems. 7.14 lbs of M-alkalinity are destroyed per lb of ammonia-nitrogen oxidized.

Temperature requirements for Nitrification
Nitrification is inhibited at lower wastewater temperatures.   Up to five times as much detention time may be needed in the winter versus the summer months since the activity drops significantly. During winter months, increasing MLVSS, MCRT will help as well as lowering wasting. A desired range is 60° to 95° degrees F. Below 40 nitrification will probably not occur.

Nitrogenous Food requirements for Nitrification
BOD5/TKN Ratio -The fraction of nitrifying organisms decreases as this ratio increases. Many times influent TKN is not measured. Refineries and Chemical plants often have amines in the influent and are used to measuring this and accounting this in the total nitrogen balance. Municipals are not used to doing this, but probably should if they have any industrial pretreatment adding to their influent, or if they have a ton of food plants or restaurants adding high loading to their plant. Many times the new cleaning and sanitation compounds have quartinary amines and biocides as a component of the cleaning

and sanitizing compounds. These can add a significant loading to the plant. Especially since it takes time to break down the amines first, before the ammonia is released and can be recognized or utilized by the nitrifiers.

Detention Time requirements for Nitrification
The time required for nitrification is directly proportional to the amount of nitrifiers present. Because the rate of oxidation of ammonia is essentially linear, short-circuiting must be prevented. Minimum detention time is approx. 4 hours at 22 ° to 24°C. Many plants run very old sludge ages. Be careful of this. A sludge age that is too old will have problems with sudden changes in the influent and will have a higher problem with toxicity issues than a medium to old sludge. Let as much of the ammonia removal happen by the carbonaceous bacteria first, and use your nitrifiers as a final polishing only.

MCRT, F/M, or Sludge Age requirements for Nitrification - When reviewing the performance of your activated sludge process for the selection of an optimum F/M ratio, MCRT, oxygen requirements, etc. , the requirements of the nitrification microorganisms must be taken into account in addition to that of the heterotrophic (carbon degrading) bacteria.

Inhibition to nitrification by Toxic compounds
Many compounds can be toxic to nitrifiers. Cooling tower biocides have many amines also present in them as well as zinc that can be toxic to the nitrifiers. Check your MSDS sheet on the chemicals used onsite.
Soluble Carbonaceous BOD > 25 mg/l in final effluent
High pH (both Nitrosomonas and Nitrobacter are inhibited by un-ionized ammonia (NH_3). Since Nitrosomonas is more sensitive than Nitrobacter, the result may be a high level of NO_2- in the final effluent.
Heavy Metals 3 mg/L to 23 mg/L
-silver, mercury, nickel, chromium, copper, zinc
Halogenated Solvents 0 mg/L
Phenol and Cresol   <20 mg/L
Cyanides <20 mg/L
**Nitrite nitrogen concentrations greater than 20 mg/l can be inhibitory towards *Nitrosomonas.*
Salinity does not appear to inhibit the nitrification process.
Chlorides do not appear to be toxic unless very high. Typical chlorides concentrations were in the range 1000-2000mg/l. Tests with concentrations as high as 4000mg/l did not show a measurable inhibition of the nitrification process.

Denitrification:
This is the process where the nitrates are used as an alternate oxygen source for the carbonaceous bacteria to consume BOD but under anoxic conditions using the nitrate as source of O instead of free oxygen in the water. It is slower than the oxygen reaction. The main issue with denitrification is it presents a chicken or the egg solution. You cannot get the nitrates until you convert the ammonia to nitrates, but usually that does not happen until the end of the cycle in the aeration basin. When you finally convert the ammonia, you usually are also out of BOD. The bacteria need BOD in order to use the nitrates. So it becomes a complicated catch-22 situation in many wastewater plants. Easy to do in theory in a research lab, but in a dynamic situation in the field in real plants, it oftentimes is tricky to completely do very easy every day.

In order by decreasing energy yield:

Aerobic $AH_2^* + O_2^\bullet \longrightarrow CO_2 + H_2O + energy$

               $AH_2 + NO_3^- \longrightarrow N_2\uparrow + H_2O + energy$

facultative $AH_2 + SO_4^{2-} \longrightarrow H_2S\uparrow + H_2O + energy$

               $AH_2 + CO_2 \longrightarrow CH_4\uparrow + H_2O + energy$

Anaerobic $AH_2 + B^{**} \longrightarrow BH_2^{***} + A + energy$
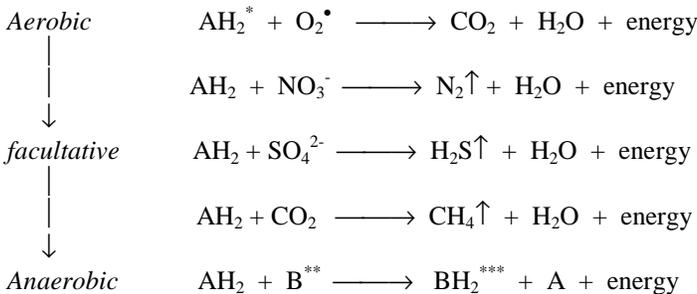
$\bullet$ dissolved oxygen
* energy stored in organic matter
** an oxidized organic compound
*** a reduced organic compound

Gassing

Phosphorus Precipitation and Removal

Some states have effluent guidelines for the discharge of phosphorus into streams, rivers, and lakes to prevent a large bloom or eutrophication. A phosphorus removal process may be needed to meet these guidelines. On the other hand, phosphorus is a critical nutrient for biological treatment processes, usually required in the proportion of 1 part as phosphorus per 100 parts BOD5 applied. For some wastes, it is necessary to add phosphorus (usually in the form of phosphoric acid) to supplement the phosphorus available in the wastewater to sustain the biological treatment process.

This section discusses the chemistry of phosphorus removal. Phosphorus addition to biological treatment processes is discussed later in this technical manual.

Chemistry of Phosphorus

As water-soluble compounds, phosphorus substances are seldom found in nature in concentrations greater than 10-4 moles except where discharged by man. In nature, phosphorus and its compounds are interrelated and interdependent on the dissolution, transport, distribution, precipitation, and accumulation of aluminum, calcium, iron, and manganese.

Phosphorus occurs in nature almost exclusively as phosphate, the fully oxidized state. It occurs in all known minerals as orthophosphate, PO_4^{-3}.

Manmade condensed inorganic phosphates have been used in synthetic detergents as builder compounds; as water softening compounds (sequesterants for calcium and magnesium hardness); peptizing agents, emulsifiers, and dispersing agents in organic compound manufacturing; industrial cleanser ingredients; in leather tanning, dyeing, laundry work, and textile processing; and detergent additives as sodium hexametaphosphate detergents. The distribution of phosphorus compounds in waste treatment can vary. As solids in the plant effluent increase, the proportion of orthopoly-, and organic-phosphorus forms will shift, with more organic phosphorus forms being present in the solids than in the clarified supernatant.

Orthophosphate, pyrophosphate, triphosphate, and higher polyphosphate anions are capable of an extraordinary number of complex interactions with metal ions in solution to form complexes, chelates, and insoluble salts. The extent of formation of these complexes is affected by:

- Varying concentrations of phosphates and metal ions
- pH
- Presence of other substances including common anions such as sulfate, carbonate, fluoride, and other organic species.

Cations capable of forming phosphate complexes include:

Major Cations

Calcium (Ca^{+2})
Sodium (Na^+)
Magnesium (Mg^{+2})

Minor Cations

Copper (Cu^{+2})
Zinc (Zn^{+2})
Manganese (Mn^{+2})
Iron (Fe^{+3})

There are changes in theoretical solubilities of ferric phosphate ($FePO_4$) and aluminum phosphate ($AlPO_4$) when the pH is adjusted. These curves cannot be used alone to account for total phosphate in solution at equilibrium. Typically these metal ions are essential in chemical treatment of phosphate. These ions are usually found in lower concentrations than the phosphates.

Biological Nutrient Removal
Completely Removing Nitrogen from the Process Stream
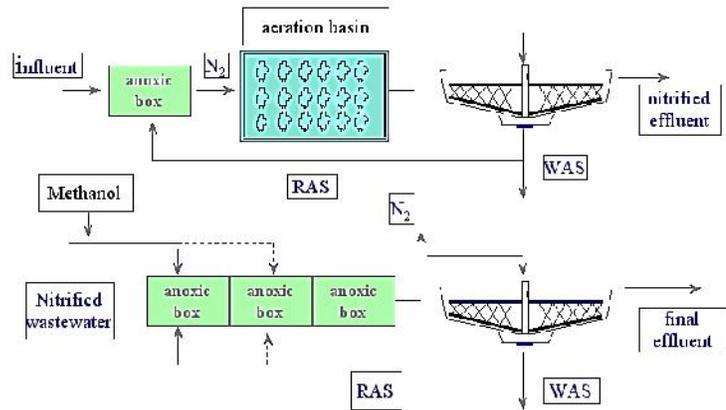
Biological Phosphorus Removal

All organisms require phosphorus for growth. The microbial activity of active organisms in biological treatment removes a significant amount of phosphorus from wastewater without chemical addition. The only form of phosphorus capable of being used by organisms is orthophosphate ((PO_4^{-3}, HPO_4^{-2}, $H_2PO_4^-$, and H_3PO_4). Therefore, to be biologically available to the microorganisms, the condensed phosphate must be hydrolyzed to orthophosphates.

There, are two mechanisms for phosphorus removal in biological treatment:

1. Chemical precipitation
2. Biological uptake

The required conditions for chemical precipitation in the biological system are as follows:
• Hydrolysis of complex phosphate to orthophosphates
• Decreasing carbon dioxide production as the waste passes through the reactor
• An increase in pH since less carbon dioxide is produced and more is being removed by aeration
• The development of conditions favorable to precipitation of calcium phosphate

Sufficient detention time is needed for these conditions to be satisfied, favoring long biological reactors.

While all biological treatment will remove phosphorus to some extent, under ideal conditions the microorganisms in activated sludge will remove more phosphorus than required for their growth. This is known as "luxury uptake" of phosphorus. It is possible to take advantage of this phenomenon by handling the activated sludge in such a way as to prevent the resolubilization of the adsorbed phosphate.

Conditions favoring luxury uptake of phosphorus in activated sludge are:

• Maintaining high dissolved oxygen (>2.0 mg/l) in all portions of the treatment process (including the secondary clarifier)

• Rapid removal of settled mixed liquor (return sludge) from the secondary clarifier (30 minutes in sludge blanket)

• Maintaining high pH (pH> 8.5) in the aeration basin and secondary clarifier can be inhibitive to the biomass and reduce the BOD reduction efficiency of the system.

Conventional biological treatment typically removes only 50% of the raw wastes phosphate, but this will be sufficient for many plants without rigorous phosphate discharge standards. Encouraging luxury uptake may allow a plant to meet stricter effluent guidelines; however, in states where 90-95% removal is required, only a combination of chemical precipitation and biological treatment will be sufficient.

Phosphorus Accumulating Organisms (PAOs). These are likely to comprise a variety of bacterial subpopulations including Acinetobacter, Rhodocyclus and some morphologically identified coccus-shaped bacteria with a diameter of about 1.2 ìm.

The EBPR process (see figure 2) works by providing an anaerobic zone with an ample supply of readily
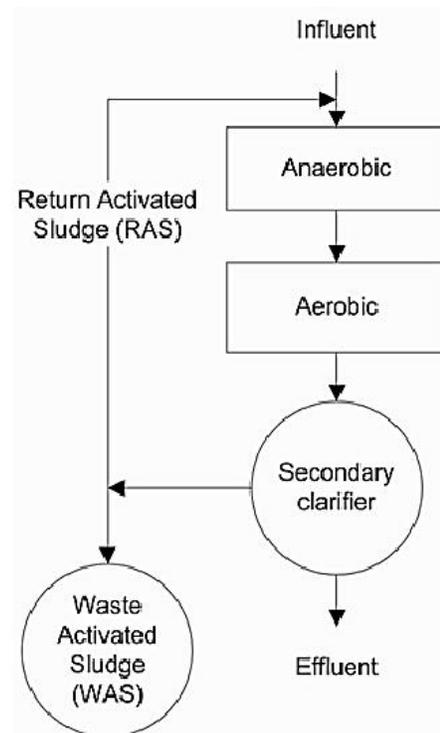

Figure 2. Anaerobic/Aerobic EBPR Process

biodegradable carbonaceous oxygen demand (rbCOD). Organic matter in the anaerobic zone is fermented to
create a source of volatile fatty acids (VFAs), particularly acetate and propionate, which in turn serve as food
sources for PAOs.

RAS in nitrifying systems designed to remove ammonia
will contain significant nitrate concentrations that are not
compatible with two stage (aerobic/anaerobic) EBPR
systems. In these cases provisions must by made to
denitrify the return solids to avoid compromising the integrity of the
anaerobic zone. Various de-nitrification EBPR configurations are effective for these conditions,
most often including one or more anoxic phases (see Figure 3) where
bacterial respiration is dependent on oxygen derived from nitrites or nitrates
rather than dissolved oxygen.

Figure 3. Anaerobic/Anoxic/Aerobic Process

Potential Effluent Quality

Effluent wastewater phosphorus concentrations can be divided into two
components: 1. Soluble phosphorus: the fraction that is available for
biological uptake in an EBPR system. 2. Particulate phosphorus: the fraction
that is subject to settling and flocculation. An efficient EBPR system followed
by good final clarification can achieve effluent phosphorus concentrations of
0.7 mg/L if sufficient VFAs are available in the process. Lower effluent concentrations down to 0.1 mg/L can be achieved
through supplemental chemical treatment and advanced effluent filtration techniques.

Chemical Phosphorus Removal

The chemical method of phosphorus removal involves the precipitation of orthophosphates with metallic
ions such as aluminum, iron, and calcium. Polyphosphates and organic phosphates do not readily react with
metallic ions and are removed only after conversion to orthophosphates by biological treatment and
hydrolysis, followed by chemical precipitation. However, as noted earlier, small amounts of polyphosphates
and organic phosphates may be removed through absorption on the floc formed by the precipitation products
of the metal ions.

Aluminum Compounds for Phosphorus Precipitation - Aluminum ions can combine with phosphate ions to
form aluminum phosphate, which precipitates as follows:

$$Al^{+3} + PO_4^{-3} \longrightarrow AlPO_4$$
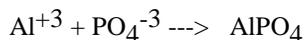
The theoretical solubility of aluminum phosphate compounds is shown as a function of pH. This solubility
curve applies to the use of aluminum sulfate (alum) as well as sodium aluminate. Aluminum Sulfate (Alum)
- Alum is hydrated aluminum sulfate with the approximate formula of $Al_2(SO_4)_3 \cdot 14H_2O$. Equation 2
shows the reaction with phosphate.

$$Al_2(SO_4)_3 \cdot 14H_2O + 2PO_4^{-3} \longrightarrow 2AlPO_4 + 3SO_4^{-2} + 14H_2O$$

Based on this equation, the stoichiometric requirement of alum per pound of phosphorus may be calculated as follows:
Molecular weight:

$Al_2(SO_4)_3 \cdot 14H_2O$ = 594 g/mole

PO_4^{-3} = 95 g/mole

$AlPO_4$ = 122g/mole

Weight ratio of alum to phosphorus:
Mole ratio Al:P = 1:1
Weight ratio Al:P = 27:31 - 0.87
% AI in alum - 54/594 - 9.1%

Therefore, alum required per gram of P
= 0.87/0.091 = 9.6 gram

In practice, a higher amount of alum is required because of a competing reaction: the neutralization of alkalinity and the precipitation of $AI(OH)_3$.

This occurs as follows:
$$AI_2(SO_4)_3 + 6HCO_3^- \longrightarrow 2AI(OH)_3 + 6CO_2 + 3SO_4^{-2}$$
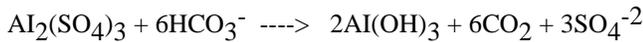
The neutralization of HCO3- ("M" alkalinity) and increase in acidity act to decrease pH and shift the wastewater alkalinity balance to absorb more carbon dioxide in solution as carbonic acid (H2CO3).
This destruction of alkalinity* can be very significant in terms of inhibiting biological activity when the biological process is operating in ammonia oxidation (nitrification).
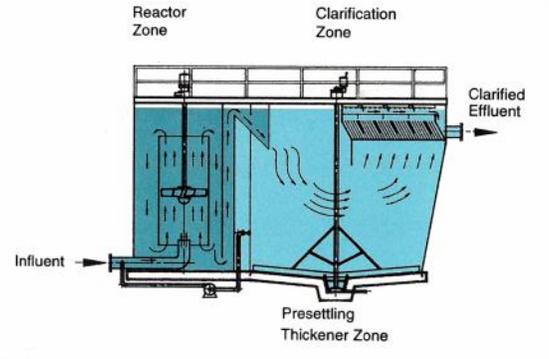
Table 6 - Equivalent mass addition relationships for alum as phosphate removal chemical*

Phosphorus Reduction Required, %	Al:P mole ratio	Al:P wt. ratio	Alum:P, wt. ratio	"M" Alkalinity Destroyed wt. ratio	Equivalent Acidity Added, ** wt. ratio
75	1.38:1	1.2:1	13:1	0.15	0.60
85	1.72:1	1.5:1	16:1	0.18	0.75
95	2.3:1	2.0:1	22:1	0.25	1.00

Table 6 summarizes the recommended alum requirements for specific levels of phosphorus removal based on a typical municipal wastewater containing 20-30 mg/l phosphate (6-10 mg/l as P) and 200-300 mg/l alkalinity as CaCO3. For wastewater with significantly different phosphorus and/or alkalinity amounts, use the stoichiometric relationships of Equations 2 and 3. For example, to achieve 95% phosphorus removal for wastewater containing 10 ppm of phosphorus, the alum dosage would be: (22) (10ppm) = 220 ppm

An anionic flocculant can be used in conjunction with alum after neutralization to help meet low aluminum concentration in the effluent. Adjustments to the pH may be necessary for the anionic flocculants to be effective. A cationic coagulant can be effective for coalescing alum solids when the pH is less than 5.5 (before neutralization).

Sodium Aluminate - Sodium aluminate (Na2A12O4), an alkaline metal salt, serves as a source of aluminum ion. Equation 4 shows the reaction with phosphate:
$$Na_2Al_2O_4 + 2PO_4^{-3} + 4H_2O \longrightarrow 2AlPO_4 + 2NaOH + 6OH^-$$
Based on Equation 4, the stoichiometric requirement of sodium aluminate per pound of phosphorus may be calculated:
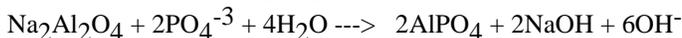
Molecular weight
$Na_2AI_2O_4$ = 164 g/mole

PO_4^{-3} = 95 g/mole

$AlPO_4$ = 122 g/mole

Weight ratio of sodium aluminate to phosphorus:

Mole ratio AI:P - 1:1
Weight ratio Al:P = 27:31 = 0.87:1
% AI in sodium aluminate = 54/164 = 32.9%

There, sodium aluminate required per gram of P = 0.87/0.329 = 2.64 grams
As in the case of alum, carbonate species compete with the phosphates for aluminum ion. Therefore, the practical dosage will be somewhat different from the theoretical dosage.

$$Na_2AI_2O_4 + 2CO_2 + 4H_2O \quad \text{---}\!\!> \quad 2Na^+ + 2HCO_{3-} + 2AI(OH)_3 \qquad (5)$$
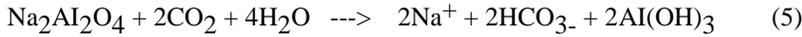
Since CO_2 is neutralized and $HCO-3$ ("M" alkalinity) increases, pH will increase slightly, depending on the amount of aluminate added.

Table 7 describes the recommended aluminate requirement for comparable levels of phosphorus removal. The basis of the calculations is the same, with total phosphorus of 6-10 mg/l as P, and "M" alkalinity as 200-300 mg/l as CaCO3.

Table 7 - Equivalent mass addition relationships for sodium as phosphate removal chemical*

Phosphorus Reduction Required, %	Al:P mole ratio	Al:P wt. ratio	Alum P:, wt. ratio	"M" Alkalinity Added, wt. ratio	Equivalent Acidity Added, ** wt. ratio
75	1.38:1	1.2:1	3.65:1	0.91	0.24
85	1.72:1	1.5:1	4. 65:1	1.14	0.15
95	3.3:1	2.0:1	6. 80:1	1.52	0.00

To achieve a 95% removal from a wastewater containing 10 ppm phosphorus, the sodium aluminate dosage would be: (6.08)(10 ppm) = 60.8 ppm

*Each pound of phosphate precipitation neutralizes 1.5 pounds of "M" alkalinity and adds 3.15 pounds of acidity as $CaCO_3$ in the form of sulfate SO_4^{-2}.

This dosage would be most effective in a pH range of 7-8. Addition of sodium aluminate will raise the pH of wastewater since it is an alkaline metal salt. The extent of the pH rise will depend on the amount of alkalinity present. Therefore no alkalinity adjustment is needed when using sodium aluminate for phosphorus removal. The use of cationic coagulant to coalesce aluminum hydroxide solids is sometimes effective. At pH greater than 7, an anionic flocculant can be effective.

Iron Compounds for Phosphorus Precipitation

Both ferrous (Fe^{+2}) and ferric (Fe^{+3}) ions can be used in the precipitation of phosphorus. Common sources of iron are $FeCl_3$, $FeCl_2$, $Fe_2(SO_4)_3$, $FeSO_4$,. and pickle liquors (a waste product from metal finishing mills containing these compounds).

Iron precipitates phosphorus as follows:
$$Fe^{+3} + PO_4^{-3} \ \ ---> \ \ FePO_4$$
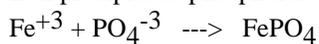
The theoretical ratio of iron (Fe^{+3}):P is 1.8:1. The dosage for the various forms of iron can be calculated. As with alum, excess dosage will be required due to any other compounds present in the wastewater that iron will also have an affinity for.

Iron (acid metal salts) lowers the pH of the water by neutralizing alkalinity. Pickle liquor depresses pH the most because it contains substantial amounts of usually unneutralized free sulfuric and/or hydrochloric acid.

Typical Strengths

	% Active	% Fe	lbs-Fe/gal
Ferrous chloride --$FeCl_2$	22-26	10-11	1.0-1.1
Ferrous sulfate -- $FeSO_4$	13-15	5-6	0.5-0.6
Ferric chloride -- $FeCl_3$	38-42	12-14	1.3-1.5
Ferric sulfate -- $Fe_2(SO_4)_3$	36-40	10-12	1.2-1.4

Ferrous salts:	Precipitation:	$2\ FeCl_2 + 2\ H_2S < == > 2\ FeS + 4\ HCl$
Ferric salts:	Step-1 (Oxidation):	$2\ FeCl_3 + H_2S ----> S_0 + 2\ FeCl_2 + 2\ HCl$
	Step-2 (Precipitation):	$2\ FeCl_2 + 2\ H_2S < == > 2\ FeS + 4\ HCl$

The equation governing iron neutralization of alkalinity is:
Hydroxide Precipitation:
$$Fe^{+3} + 3H_2O ---> Fe\ (OH)_3 + 3H^+$$
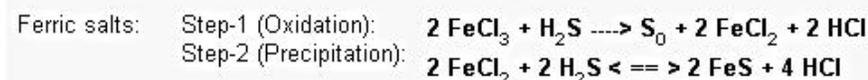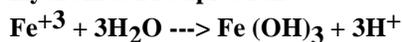
Iron compounds have their preferential solubility pH range, as do aluminum salts. The optimum pH range for $FePO_4$ is 4.5 - 5.5, although the minimum solubility of $Fe(OH)_3$ is not attained until pH 7-8. The addition of 3 moles of acidity per mole of iron salt added at pH 7 will consume 2.69 equivalent parts of "M" alkalinity per part of Fe^{+3} added, and 1.79 equivalent parts of "M" alkalinity for each part of Fe^{+2} added.

Unfortunately, simultaneous secondary reactions can occur, requiring additional quantities of precipitating agent.
These competing reactions are:
1. Creation of hydroxides (responsible for low sludge index)
Fe3+ + 3Cl- + 3OH- + 3H+ ð Fe(OH)3 + 3HCl
2. Complex reactions with organic substances.
3. Absorption reactions.
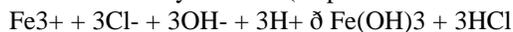
Alkalinity is also critical for metal hydroxide formation.
Ferric and aluminum salts are added to induce coagulation by the formation of metal hydroxide recipitates. Figure 8.2 indicates an optimum pH for each metal hydroxide. The addition of either aluminum or iron salts depresses the pH due to production of hydrogen ions, as shown in Equations 8.1 and 8.2. The limit of pH depression is a function of the dosage and the buffering capacity or alkalinity of the water, in particular the carbonate concentration. If there is insufficient alkalinity to buffer the effect of the chemical, a buffering chemical such as sodium bicarbonate is added. The addition of aluminum and iron coagulants may therefore be of concern with low alkalinity water.

 In an anaerobic environment where a byproduct is H2S, interference with ferric precipitation of phosphorus also occurs. Many EQ tanks may wind up anaerobic, or during forced BNR treatment, where anaerobic process are brought about for nutrient removal, ferric addition afterwards does not always work, and an overdose of ferric compounds can occur.

Lime for Phosphorus Precipitation

Calcium ion reacts with phosphate ion in the presence of hydroxyl ion to form hydroxyapatite, a form of calcium phosphate. Calculating an approximate dosage for phosphorus removal is possible using mass balance, as was done for alum. However, it is generally not necessary because lime dose is largely determined by alkalinity reactions similar to those in lime softening that take place when the pH is raised.

The reaction of lime with phosphate is pH dependent. The solubility of hydroxyapatite is low. At a pH of 9, a large fraction of the phosphorus can be removed. In lime treatment of wastewater, the operating pH is often determined by the pH required to obtain good suspended solids removal, and as long as pH exceeds 9.0, good phosphorus removal will generally follow.

The total amount of spent lime sludge to be handled is more than 2.25 times the amount for sodium aluminate. The amount of effluent calcium as Ca^{+2} will increase 33% (20 mg/l), and the effluent alkalinity will be increased by 430 mg/l as $CaCO_3$.

Anytime chemicals such as lime, alum or ferric compounds are used, significant impact on sludge, and all the typical calculations in a wastewater treatment plant are impacted. F/M, mlss, solids, even settling times, since the chemicals weigh down the normal floc and cause the sludge to settle faster. Be careful if you need to use chemicals to supplement your biological treatment plant. Final polish with a separate clarifier and sand filter are the optimum, that way, they do not impact the biological portion of the system.

Microscopic analyses: Using the microscope becomes more critical when using any chemicals in the wastewater treatment system, since not only can inorganic solids be generated, they can mix with the normal biological solids, and change the biomass ratios.   <u>**Here are a few different plants that had ferric in their water.**</u>

These are from 4 different wastewater treatment plants. As you can see the ferric can impact the biomass. In the first photo, the ferric is working as a coaggulant, and pulls the floc into long, irregular shapes. The second, the ferric shows up as a reddish color compared to the normal clear or brown floc structures. The bottom two plants both had high levels of zooglea present and one also had high levels of Type 021N, which indicates a nutrient deficiency, in this case phosphorus, since the ferric has a very high affinity for phosphorus. It is ok to remove excess phosphorus in the final effluent, but your biomass does need some in the normal process, or you will select for filaments and zooglea, which in turn can impact solids handling, dewatering and settling.

As you can see there are many options for nutrient removal. Many are costly and generate quite a bit of sludge. Normal operations will have to be modified and typical wastewater methods will need to be adjusted, since all normal mass balance calculations will be thrown off. It is critical that you use the microscope to see how the chemicals impact the floc structures, as well as the higher life forms.